Application No.: 10/719162
Docket No.: FL0233USNA   Page 5

REMARKS

For ease in following the attached Remarks, the reference numbers of the May 16, 2007 Office Action are used herein.

1. Applicant acknowledges acceptance of the compliant amendment.

Specification:

5 and 7. In the specification on page 1, line 2, the title has been amended in accordance with Applicant's proposed title change set forth on page 5 of the remarks filed November 22, 2006 that the Examiner found acceptable.

35 USC 103:

6 and 9. Claims 1-8 have been rejected under 35 USC §103 as being unpatentable over Honda et al. (US 4,916,146 A) in view of Kawasaki et al. (US 5,782,730 A). Applicant disagrees.

Claim 1 has been amended to clarify the composition use for rotolining. This is supported by lines 5-7, on page 1 of the specification.

In claim 1 of the present invention, it is disclosed that the composition is "melt flowable". This is in contrast, to the polytetrafluoroethylene (PTFE) dispersion composition disclosed in Honda. PTFE is not melt processible, as disclosed in Fluoroplastics Volume 1: Non-Melt Processible Fluoroplastics by Sina Ebnesajjad, Plastics Design Library, Norwich NY, 2002. (copy enclosed) (See the Introduction (p.1) column 1, paragraph 3, and the introduction to Chapter 4 "Fluoropolymer Monomers", which disclose that PTFE and modified PTFE (tetrafluoroethylene copolymerized with <1% of other monomers) are not melt processible.) Honda does not attempt to melt-process the polymer of his invention, rather the polymer dispersed in liquid medium is applied like a paint or other coating (US 4,914,146, column 4, lines 16-24). Furthermore, the present invention (claim 1) is for use in rotolining which is not disclosed by Honda. Additionally, in column 4, line 37, Honda discloses the "good non-adhesivity" of the heating roller. This contrasts with the present invention which discloses adhesion promotion of the present composition. Also, Honda makes reference to a composition that is aqueous (see Examples 4 and 5 in column 6). The Honda composition is in contrast to the present invention composition comprises a powder and is non-aqueous.

Additionally, the prior arguments regarding Honda from the November 22, 2006 Remarks are reiterated here as well. In the present invention, metal powders such as aluminum are taught away from use in the present invention because such metal promotes bubbling in the lining during formation. (See page 3, lines 20-22.) This is in contrast to

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Honda. The Examiner states on page 5, that "Honda does not explicitly teach that the metal powder is an adhesion promoting, non-bubble promoting metal powder". Furthermore, Honda discloses in column 3, line 59 the use of aluminum. Thus, for the above stated reasons, Honda does not teach the adhesion promoting, non-bubble promoting metal powder composition of the present invention.

Kawasaki teaches the use of metal powder (see col 7, lines 30-32) in reference to the elastic layer of the pressure roller, which is silicone rubber. Silicone rubber is not a fluoropolymer and is not melt processable, as disclosed in Principles of Polymerization 3rd edition, by George Odian, Wiley-Interscience, New York NY 1991, pp. 138-140, polymerization be described in the last paragraph on p. 139. (copy enclosed) Furthermore, Odian discloses at p.138 fourth line from the bottom,, and it is well-known, that silicone is an excellent adhesive, so one does not learn from Kawasaki's use of metal powder in silicone, that metal powder would confer adhesion-promoting properties on melt-processible fluoropolymer. Thus, Kawasaki does not teach adding the metal powder to the fluororesin top layer but rather to silicone. Hence, Applicant contends it would not have been obvious to combine Honda et al. with Kawasaki et al. because they do not disclose the use of a melt flowable composition for rotolining. Furthermore, it would not have been obvious to combine Honda, which teaches away from an adhesion promoting, non-bubble promoting metal powder composition, to Kawasaki, which teaches the use of metal powder in silicone rather than fluoropolymer, to obtain the present invention. Hence, there is no motivation to combine these references. For these reasons, claim 1, as amended, is believed to be in allowable condition.

Claims 4-6 are dependent from claim 1 and thus believed to be non-obvious for the same reasons as claim 1.

Applicant contends that claim 2 and 3 are dependent from claim 1, and thus are believed to be in allowable condition for the above reasons regarding claim 1.

Applicant contends that claim 7 is dependent from claim 1, and thus is believed non-obvious for the above stated reasons regarding claim 1.

Claim 8 is dependent from claim 1 and thus believed to be in allowable condition for the above stated reasons regarding claim 1.

No petition under 37 CFR § 1.136 for an extension of time to respond to the Examiner's action is believed required. However, should a fee be required for consideration of this fee, please charge that to Deposit Account No. 04-1928 (E.I. du Pont de Nemours and Company.)

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In view of the foregoing, allowance of the above-referenced application is respectfully requested.

Respectfully submitted,

Tamera L. Fair

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Dated: August 13, 2007

Enclosures: "Fluoroplastics"
                    "Principles of Polymerization"

Fluoroplastics

Volume 1: Non-Melt Processible Fluoroplastics
The Definitive User's Guide and Databook

Sina Ebnesajjad

(pdl)

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Manufactured in the United States of America.

Introduction

It is hard for most people to imagine what the world would be like without plastics. It is equally difficult for many design engineers to envision designing projects without the availability of fluoropolymers. Only expensive exotic metals can replace the chemical inertness of these plastics to highly corrosive and aggressive substances. Even though some engineering plastics can stand up to temperatures as well as fluoropolymers, they suffer major property losses beyond their glass transition temperatures. Engineering plastics lack the chemical inertness and low friction characteristics of fluoropolymers. No other material offers the low coefficient of friction of fluoropolymers.

Fluoropolymers have evolved over six decades. New monomers have allowed the synthesis of new polymers with new methods of processing. Most newer perfluoropolymers have the same basic properties as polytetrafluoroethylene (PTFE) but they offer new methods of processing. These new techniques have greatly increased the range of parts that can be fabricated from fluoropolymers at reduced cost. Today, fluoropolymers are processed by methods almost identical to those used a half century ago as well as by state of the art molding technologies.

This book is the first of two volumes about fluoropolymers. The division of the volumes is based on the processing techniques of commercial fluoropolymers. Homopolymers of tetrafluoroethylene (TFE), the main building block or "monomer" for polytetrafluoroethylene plastics are processed by nontraditional techniques. The extremely high melt viscosity of TFE polymers precludes their processing by conventional melt processing methods such as injection molding and melt extrusion. Copolymers of trace amounts of other perfluorinated monomers with TFE known as *Modified PTFE* are covered in this book because they are processed by the same techniques. Copolymers of TFE with extensive comonomer contents are handled by melt-processing methods. Volume One is mainly devoted to exploring the various homopolymers of tetrafluoroethylene and chlorotrifluoroethylene. Polychlorotrifluoroethylene (PCTFE) plastics, which can be processed by non-melt processing and some melt-processing techniques, have been covered in Volume One.

All aspects of the fluoropolymers including monomer synthesis, polymerization, properties, applications, part fabrication techniques, safety in handling, and recycling are discussed. Homopolymers and copolymers of vinylidene fluoride, all melt processible, have been covered in Volume Two because of the close resemblance of polyvinylidene fluoride in composition and in processing techniques to melt processible copolymers of tetrafluoroethylene. Polyvinyl fluoride (PVF) which is processed by melt processing of its dispersion in a polar solvent has also been covered in Volume Two.

Fluoropolymers have outstanding chemical resistance, low coefficient of friction, low dielectric constant, high purity, and broad use temperatures. Most of these properties are enhanced with an increase in the fluorine content of the polymers. For example, polytetrafluoroethylene, which contains four fluorine atoms per repeat unit, has superior properties compared to polyvinylidene fluoride, which has two fluorine atoms for each repeat unit. Generally, these plastics are mechanically weaker than engineering polymers. Their relatively low values of tensile strength, deformation under load or creep, and wear rate require the use of fillers and special design strategies. This book addresses ways of overcoming these shortcomings.

The primary objective in every section is to facilitate comprehension by a reader with a modest background in science or engineering. There are a number of measurement methods and techniques which are unique to fluoropolymers. In each case, these methods are defined for the reader. The book is divided into three parts; each part consists of several chapters. Each chapter has been written so it can be consulted independently of the others.

The first part of the book deals with definitions and fundamental subjects surrounding the polymerization of fluoropolymers. Basic subjects such as the identification of fluoropolymers, their key properties, and some of their everyday uses are addressed. The main monomer, tetrafluoroethylene, is extremely flammable and explosive. Consequently, safe polymerization of this monomer requires special equipment and technology. Molecular forces within these polymers are reviewed and connected to macro properties. Monomor and polymer synthesis techniques and properties are described. Part One ends with a detailed list of advertised commercial grades of various forms of PTFE and PCTFE.

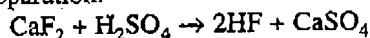# 4 Fluoropolymer Monomers

4.1 Introduction

In this chapter, synthesis and properties of major monomers for polymerization of non-melt processible fluoroplastics are discussed, including those used to modify the homopolymers. Tetrafluoroethylene is the primary monomer for polytetrafluoroethylene (PTFE) preparation. Small amounts (<1%) of other monomers are incorporated in the PTFE structure to modify its properties and processing characteristics. These monomers include hexafluoropropylene (HFP), perfluoroalkylvinylethers (PAVE), and chlorotrifluoroethylene (CTFE). CTFE is homopolymerized to produce the polychlorotrifluoroethylene (PCTFE) family of resins. A number of specialty monomers, though less common, are also used to modify the PTFE structure. Examples include perfluoroisopropyl vinyl ether and perfluorobutyl ethylene.
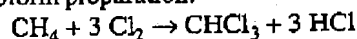
4.2 Synthesis of Tetrafluoroethylene

Tetrafluoroethylene ($CF_2=CF_2$) is the main building block of all perfluorinated polymers, that is, polymers comprised of carbon, fluorine and occasionally a small amount of oxygen. It is difficult to establish exactly the first successful synthesis. Publications in 1890's report a variety of attempts to synthesize TFE by direct reaction of fluorine with carbon, fluorine with chloromethanes and tetrachloroethylene with silver fluoride.[1]-[4] The data presented are insufficient to determine that these efforts actually lead to TFE. Humiston[5] reported the first documented preparation of TFE in 1919 which has been disputed due to erroneous property data.

The first reliable and complete description of synthesis was published in 1933 by Ruff and Bretschneider[6] in which they prepared TFE from decomposition of tetrafluoromethane in an electric arc. Separation of TFE was accomplished by bromination followed by dehalogenation with zinc to purify TFE from the pyrolysis products. Numerous other papers have reported synthesis of tetrafluoroethylene. The works that report commercially significant techniques for TFE preparation list fluorspar (CaF$_2$), hydrofluoric acid and chloroform as the starting ingredients.[7]-[14] The reaction scheme is shown below:
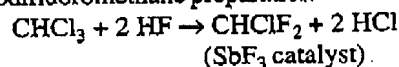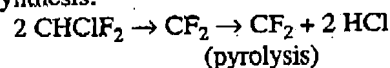
HF preparation:
$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

Chloroform preparation:
$$CH_4 + 3\ Cl_2 \rightarrow CHCl_3 + 3\ HCl$$

Chlorodifluoromethane preparation:
$$CHCl_3 + 2\ HF \rightarrow CHClF_2 + 2\ HCl$$
$$(SbF_3\ catalyst)$$

TFE synthesis:
$$2\ CHClF_2 \rightarrow CF_2 \rightarrow CF_2 + 2\ HCl$$
$$(pyrolysis)$$

A few other side compounds are also produced during pyrolysis including hexafluoropropylene, perfluorocyclobutane and octafluoroisobutylene, 1-chloro-1,1,2,2-tetrafluoroethane, 2-chloro-1,1,1,2,3,3-hexafluoropropane and a small amount of highly toxic perfluoroisobutylene.

Sherratt[15] has provided a detailed description of preparation of TFE. The overall yield of TFE production depends on the pyrolysis reaction. It proceeds to yield better than 90% TFE at short contact times, low conversions and subatmospheric pressure in the temperature range of 590–900°C. Results similar to subatmospheric pyrolysis can be achieved if superheated steam is present during the pyrolysis. Tetrafluoroethylene yields approaching 95% can be achieved at 80% chlorodifluoromethane conversion if the molar ratio of steam to CHClF$_2$ is in the range of 7:1 to 10:1.

The products of pyrolysis are cooled, scrubbed with a dilute basic solution to remove HCl and dried. The resulting gas is compressed and distilled to recover the unreacted CHClF$_2$ and to recover high purity TFE.[15] Polymerization of tetrafluoroethylene to high molecular weight requires extreme purity requiring removal of all traces of telogenic hydrogen or chlorine-bearing impurities. Tetrafluoroethylene can autopolymerize if it is not inhibited. Effective TFE autopolymerization inhibitors include a variety of terpenes, such as α-pinene, Terpene B, and d-limonene[16] which appear to act as scavengers of oxygen, a polymerization initiator.

Tetrafluoroethylene is highly flammable and can undergo violent deflagration in the absence of air:

$$C_2F_4 \rightarrow C + CF_4$$
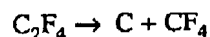
Heat of reaction values between 57–62 kcal/mole (at 25°C and 1 atm) have been reported for TFE

PRINCIPLES OF POLYMERIZATION

Third Edition

GEORGE ODIAN
The College of Staten Island
The City University of New York
Staten Island, New York

A Wiley-Interscience Publication

JOHN WILEY & SONS, INC.
New York / Chichester / Brisbane / Toronto / Singapore

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higher temperatures are avoided because polyurethanes undergo several different types of degradation reactions, such as

$$\sim\sim NH-COO-CH_2CH_2\sim\sim \rightarrow \sim\sim NH_2 + CO_2 + CH_2=CH\sim\sim \qquad (2\text{-}190)$$

$$\sim\sim NH-COO-CH_2CH_2\sim\sim \rightarrow CO_2 + \sim\sim NH-CH_2CH_2\sim\sim \qquad (2\text{-}191)$$
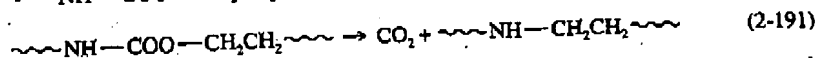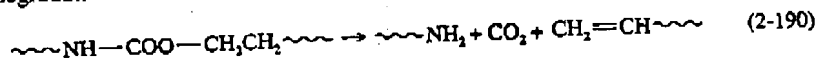
as well as decomposition back to the alcohol and isocyanate monomers. Overall control in the synthesis of polyurethane foamed products also requires a balance between the polymerization–crosslinking and blowing processes. An imbalance between the chemical and physical processes can result in a collapse of the foamed structures (before solidification by crosslinking and/or cooling) or imperfections in the foam structures, which yields poor mechanical strength and performance.

The wide variations possible in synthesis give rise to a wide range of polyurethane products including flexible and rigid foams and solid elastomers, extrusions, coatings, and adhesives. Polyurethanes possess good abrasion, tear, and impact resistance coupled with oil and grease resistance. More than 2 billion pounds of polyurethane products are produced annually in the United States. Flexible foamed products include upholstered furniture and auto parts (cushions, backs, and arms), mattresses, and carpet underlay. Rigid foamed products with a closed-cell morphology possess excellent insulating properties and find extensive use in commercial roofing, residential sheathing, and insulation for water heaters, tanks, pipes, refrigerators, and freezers. Solid elastomeric products include forklift tires, skateboard wheels, automobile parts (bumpers, fascia, fenders, door panels, gaskets for trunk, windows, windshield, steering wheel, instrument panel), and sporting goods (golf balls, ski boots, football cleats). Many of these foam and solid products are made by reaction injection molding (RIM), a process in which a mixture of the monomers is injected into a mold cavity where polymerization and crosslinking take place to form the product. Reaction injection molding of polyurethanes, involving low-viscosity reaction mixtures and moderate reaction temperatures, is well suited for the economical molding of large objects such as automobile fenders. (Many of the elastomeric polyurethane products are *thermoplastic elastomers*; see Sec. 2-13c.)

2-12f Polysiloxanes

Polysiloxanes, also referred to as *silicones*, possess an unusual combination of properties that are retained over a wide temperature range (-100 to $250°C$). They have very good low temperature flexibility because of the low T_g value ($-127°C$). Silicones are very stable to high temperature, oxidation, chemical and biological environments, and weathering and possess good dielectric strength, and water repellency. Almost 0.5 billion pounds of polysiloxanes are produced annually in the United States in the form of fluids, resins, and elastomers. Fluid applications include fluids for hydraulics, antifoaming, water-repellent finishes for textiles, surfactants, greases, lubricants, and heating baths. Resins are used as varnishes, paints, molding compounds, electrical insulation, adhesives, laminates, and release coatings. Elastomer applications include sealants, caulks, adhesives, gaskets, tubing, hoses, belts, electrical insulation such as automobile ignition cable, encapsulating and molding applications, fabric coatings, encapsulants, and a variety of medical applications (antiflatulents, heart valves, en-

thanes undergo several different types
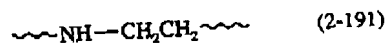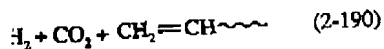
$$H_2 + CO_2 + CH_2{=}CH\sim\sim\quad (2\text{-}190)$$

$$\sim\sim NH{-}CH_2CH_2\sim\sim\quad (2\text{-}191)$$

isocyanate monomers. Overall control
ts also requires a balance between the
ses. An imbalance between the chem-
ipse of the foamed structures (before
imperfections in the foam structures,
formance.
e rise to a wide range of polyurethane
id solid elastomers, extrusions, coat-
d abrasion, tear, and impact resistance
than 2 billion pounds of polyurethane
tates. Flexible foamed products include
is, backs, and arms), mattresses, and
a closed-cell morphology possess ex-
use in commercial roofing, residential
inks, pipes, refrigerators, and freezers.
s, skateboard wheels, automobile parts
s for trunk, windows, windshield, steer-
ds (golf balls, ski boots, football cleats).
le by reaction injection molding (RIM),
rs is injected into a mold cavity where
form the product. Reaction injection
cosity reaction mixtures and moderate
conomical molding of large objects such
ieric polyurethane products are *thermo-*

possess an unusual combination of prop-
ture range (−100 to 250°C). They have
of the low T_g value (−127°C). Silicones
n, chemical and biological environments,
strength, and water repellency. Almost
uced annually in the United States in the
applications include fluids for hydraulics,
tiles, surfactants, greases, lubricants, and
s, paints, molding compounds, electrical
coatings. Elastomer applications include
hoses, belts, electrical insulation such as
nd molding applications, fabric coatings,
lications (antiflatulents, heart valves, en-

casing of pacemakers, prosthetic parts, contact lenses, coating of plasma bottles to avoid blood coagulation). Silicone elastomers differ markedly from other organic elastomers in the much greater effect of reinforcing fillers in increasing strength properties.

Polysiloxane fluids and resins are obtained by hydrolysis of chlorosilanes such as dichlorodimethyl-, dichloromethylphenyl-, and dichlorodiphenylsilanes [Brydson, 1982; Hardman and Torkelson, 1989]. The chlorosilane is hydrolyzed with water to a mixture of chlorohydroxy and dihydroxysilanes (referred to as *silanols*), which react with each other by dehydration and dehydrochlorination. The product is an equili-
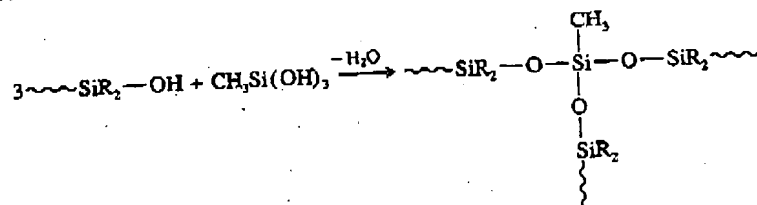

$$(2\text{-}192)$$
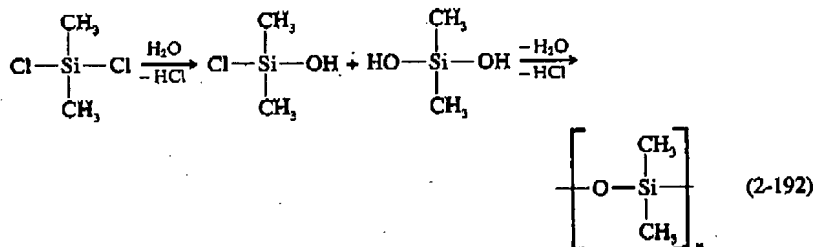
brated mixture of approximately equal amounts of cyclic oligomers and linear polysiloxanes. The amount of cyclics can vary from 20 to 80% depending on reaction conditions. The major cyclic oligomer is the tetramer with progressively decreasing amounts of higher cyclics. After the initial equilibration, a disiloxane terminating agent such as [(CH₃)₃Si]₂O is added to stabilize the reaction mixture by termination of the linear species. The process may be carried out under either acidic or basic conditions depending on the desired product molecular weight. Basic conditions favor the production of higher molecular weight. Mixtures of cyclic oligomers and linear polymer may be employed as silicone fluids, or the cyclic content may be decreased prior to use by devolatilization (heating under vacuum). The synthesis of silicone resins proceeds in a similar manner except that the reaction mixture includes trichlorosilanes to bring about more extensive polymerization with crosslinking. Typically, the polymer product will be separated from an aqueous layer after the hydrolytic step, heated in the presence of a basic catalyst such as zinc octanoate to increase the polymer molecular weight and decrease the cyclic content, cooled, and stored. The final end-use application of this product involves further heating with a basic catalyst to bring about more extensive crosslinking.

Silicone elastomers are either *room-temperature vulcanization* (RTV) or *heat-cured silicone rubbers* depending on whether crosslinking is accomplished at ambient or elevated temperature. (The term *vulcanization* is a synonym for crosslinking. *Curing* is typically also used as a synonym for crosslinking but often refers to a combination of additional polymerization plus crosslinking.) RTV and heat-cured silicone rubbers typically involve polysiloxanes with degrees of polymerizations of 200–1500 and 2500–11,000, respectively. The higher-molecular-weight polysiloxanes cannot be synthesized by the hydrolytic step polymerization process. This is accomplished by ring-opening polymerization using ionic initiators (Sec. 7-11a). "One-component" RTV rubbers consist of an airtight package containing silanol-terminated polysiloxane, crosslinking agent (methyltriacetoxysilane, and catalyst (e.g., dibutyltin laurate). Moisture from the atmosphere converts the crosslinking agent to the corresponding silanol (acetic

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acid is a by-product), $CH_3Si(OH)_3$, which brings about further polymerization combined with crosslinking of the polysiloxane.

$$3 \sim\sim SiR_2—OH + CH_3Si(OH)_3 \xrightarrow{-H_2O} \sim\sim SiR_2—O—\underset{\underset{\underset{SiR_2}{|}}{\overset{|}{O}}}{\overset{CH_3}{\overset{|}{Si}}}—O—SiR_2 \sim\sim$$

$$(2\text{-}193)$$

Two-component RTV formulations involve separate packages for the polysiloxane and crosslinking agent. Hydrosilation curing involves the addition reaction between a polysiloxane containing vinyl groups (obtained by including methylvinyldichlorosilane in the original reaction mixture for synthesis of the polysiloxane) and a siloxane crosslinking agent that contains Si—H functional groups, such as 1,1,3,3,5,5,7,7-octamethyltetrasiloxane. The reaction is catalyzed by chloroplatinic acid or other soluble
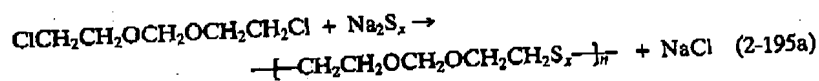
$$\sim\sim\underset{\underset{CH=CH_2}{|}}{SiR}—O\sim\sim + Si[OSi(CH_3)_2H]_4 \rightarrow$$
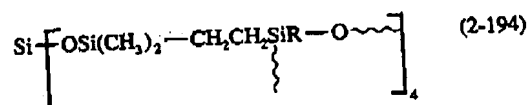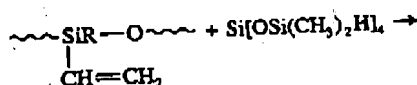
$$Si\left[OSi(CH_3)_2—CH_2CH_2SiR—O\sim\sim\right]_4 \qquad (2\text{-}194)$$

Pt compound. Hydride-functional siloxanes can also crosslink silanol-terminated polysiloxanes. The reaction is catalyzed by tin salts and involves H_2 loss between Si—H and Si—O—H groups. Heat-curing of silicone rubbers usually involves free-radical initiators such as benzoyl peroxide (Sec. 9-2c). Hydrosilation at 50–100°C is also practiced.

2-12g Polysulfides

Polysulfide elastomers are produced by the reaction of an aliphatic dihalide, usually bis(2-chloroethyl)formal, with sodium polysulfide under alkaline conditions [Brydson, 1982; Ellerstein, 1988].

$$ClCH_2CH_2OCH_2OCH_2CH_2Cl + Na_2S_x \rightarrow$$

$$\left[CH_2CH_2OCH_2OCH_2CH_2S_x\right]_n + NaCl \qquad (2\text{-}195a)$$

The reaction is carried out with the dihalide suspended in an aqueous magnesium hydroxide phase. The value of x is slightly above 2. The typical polymerization system includes up to 2% 1,2,3-trichloropropane. The polymerization readily yields a polymer with a very high molecular weight, but this is not desirable until its end-use application. The molecular weight is lowered and the *polysulfide rank* (value of x) is simultaneously brought close to 2 by reductive treatment with NaSH and Na_2SO_3 followed by acidification. The result is a liquid, branched polysulfide with terminal thiol end groups